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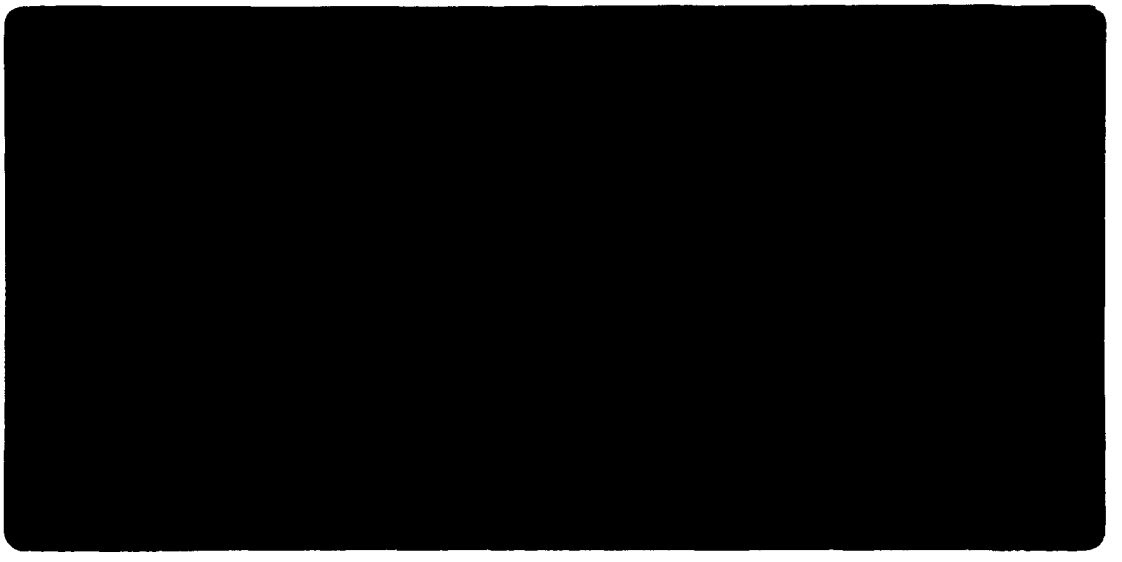

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# CHAR BED BURNING — LABORATORY STUDIES

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# Char Bed Burning - Laboratory Studies

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ABSTRACT

A laboratory char bed reactor was used to obtain quantitative data on char bed burning rates under conditions that simulate bed burning in a recovery boiler. It was found that the burning process could be treated as a series of parallel heterogeneous reactions that are mass transfer controlled at sufficiently high temperatures. Measured oxygen mass transfer coefficients from bed burning experiments were comparable with those calculated from common mass transfer correlations.

Inclusion of $H_2O$ and $CO_2$ in the $O_2$ - $N_2$ mixture supplied to the bed affected the rate of char burning. $H_2O$ catalyzes the oxidation of CO to $CO_2$ in the gas phase, so $CO_2$ was the only significant char combustion product when $H_2O$ was present. In all cases, $CO_2$ in the gas supply increased the total carbon flux from the bed. Addition of $H_2O$ vapor did not increase the carbon flux. The increased carbon removal due to the water gasification reaction was counterbalanced by the decrease in the oxygen-carbon reaction, since oxygen

reacts with CO and $H_2$ in the boundary layer. If bed temperatures are high enough, the net effect of $H_2O$ and $CO_2$ in the combustion air stream is to intensify combustion near or at the bed.

## INTRODUCTION

Char beds are a common feature of recovery boilers, consisting of combustible solids and molten or solid inorganic compounds (smelt). The main processes in char bed burning are:

1. conversion of combustible solids to gases,
2. combustion on or near the bed to release heat,
3. reduction of sulfate to sulfide,
4. liquification and transport of smelt.

In attempting to understand bed burning, the following information is considered essential:

1. proper description of the key chemistry,
2. capability to describe the rate processes and predict the effects of all significant variables on burning rates,
3. a rational basis for describing and determining bed composition and geometry.

The objectives of this paper are to describe the key issues in bed burning, summarize the available experimental results, and define the remaining information needs.

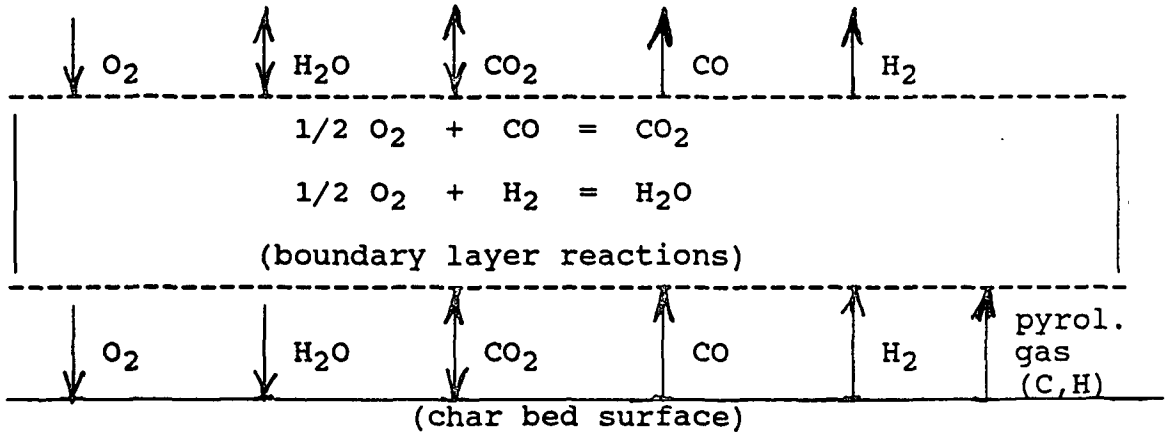
## Bed Burning Concepts

Bed burning can be treated as a series of heterogeneous chemical reactions occurring between the furnace gases above the bed and the condensed phase materials in the bed itself. With heterogeneous reactions, mass transfer of reactants to the bed and of products away from the bed can be important.

A general diagram of the chemistry of the char bed burning process is shown in Figure 1. It is evident in Figure 1 that the char bed burning is very complex. Not only are there heterogeneous reactions occurring at the bed surface but also homogeneous reactions with combustible gases coming from the bed surface. It is helpful to break up the overall process into key steps and focus on them separately.

There are four carbon oxidation reactions, with $Na_2SO_4$, $O_2$, $CO_2$, and $H_2O$ acting as oxidants. The first two reactions do not have well-defined stoichiometry, since either CO or $CO_2$ can be a product. The reaction with sulfate involves only bed constituents and acts as a homogeneous reaction. The three heterogeneous reactions of importance are with $O_2$, $CO_2$, and $H_2O$. The latter two are commonly referred to as gasification reactions.

All of the char-carbon consuming reactions have Arrhenius-type temperature dependencies, so bed temperature is the parameter that determines whether or not inherent chemical reaction kinetics determines the overall reaction




$$(1-f/2)\ O_2 + C = f\ CO + (1-f)\ CO_2$$

$$2\ O_2 + Na_2S = Na_2SO_4$$

$$Na_2SO_4 + x\ C = Na_2S + (4-x)\ CO_2 + (2x-4)\ CO$$

$$CO_2 + C = 2\ CO$$

$$H_2O + C = H_2 + CO$$

Solids + pyrolysis = (C,H) gases

(char bed reactions)

**Figure 1. Diagram of Char Bed Burning Chemistry.**

rate. At sufficiently high bed temperatures, all of the heterogeneous carbon burning reactions will become gas-side mass transfer controlled.

Mass transfer rates will depend on gas concentrations and mass transfer coefficients. Mass transfer coefficients for the different gas species will depend on the diffusivity of the component, the velocity of the gas over the bed surface, the bed surface geometry, and the gas properties. Once appropriate mass transfer coefficients can be found for one gas species, they can be generalized to other gases by using well-known correlation equations.

Oxygen moving toward the bed must pass through and can react with combustibles coming off the bed in the boundary layer close to the bed surface. The rate of reaction between oxygen and combustibles increases with temperature and is catalyzed by water vapor. Reactions between oxygen and combustibles in the gas boundary layer will modify effective concen trations of O2, CO2, and H2O, and thus will affect mass fluxes of gas species to the bed surface.

Above-bed reactions will be enhanced if the bed material is still undergoing pyrolysis. Pyrolysis is a thermally driven decomposition of liquor solids to form combustible gases and a solid phase containing char carbon and inorganic smelt constituents. When pyrolysis is complete, the remaining carbon can only react heterogeneously. Combustible pyrolysis gases

coming from the bed will scavenge oxygen above the bed and reduce or eliminate heterogeneous oxidation reactions at the bed surface.

The combination of the sulfide oxidation and sulfate reduction reactions can act as a catalytic path for carbon oxidation. If the rates of these two reactions balance, there will be no net change in the sulfur reduction state (reduction efficiency) and the only effect is burnup of carbon with oxygen. If the reduction efficiency increases during bed burning (compared to the state of the material reaching the bed), it will add to carbon consumption. If there is a net decrease in reduction efficiency, the bed will act as a sink for oxygen.

## Approach

With these considerations defined, the key information needed to describe bed burning is as follows:

1. mass transfer coefficients for one gas species as a function of gas velocity and bed geometry,

2. bed temperatures characterizing relative rates of reaction and mass transfer,

3. changes in the reduction state of the material in the bed,

4. ratios of $CO/CO_2$ for the $O_2$ - C and $Na_2SO_4$ - C reactions at the bed,

5. determination of the degree of interpenetration of oxygen and combustibles in the boundary layer above the bed,

6. determination of the rate of volatile combustibles production by pyrolysis and the effect that this has on bed burning rates.

A significant simplification in studying bed burning can be made by using beds of fully-pyrolyzed char, since the bed material consists only of solid carbon and the three inorganic compounds $Na_2CO_3$, $Na_2S$, and $Na_2SO_4$. This eliminates continued volatiles release and reaction and, in combination with a moisture-free gas supply, eliminates water vapor (and its catalytic effect on gas-phase oxidation) from the system.

The following approach was used to obtain quantitative information on char burning.

1. Char burning rates were measured with fully-pyrolyzed char and $O_2$ - $N_2$ mixtures. This allowed determination of oxygen mass transfer rates and measurements of oxygen mass transfer coefficients.

2. Carbon dioxide and water vapor were added to the gas supply to obtain information on bed burning with simultaneous oxidation and gasification.

3. No experiments were performed with incompletely pyrolyzed char. A concept for treating this complication has been developed, but it has not been experimentally verified.

4. Only burning rates were measured. No data were obtained on sulfur reduction state changes during char burning.

## EXPERIMENTAL SYSTEM

The char bed burning experiments were carried out in the char bed furnace of the black liquor flow reactor at IPST. Details of the construction of this reactor are given in References 1 and 2. All experiments were done in a batch mode using preformed beds of fully-pyrolyzed char. The combustion "air" supply was dry oxygen-nitrogen mixtures for all experiments except those specifically aimed at evaluating CO2 and H2O gasification.

The configuration of the bed burning furnace is shown in Figure 2. The char bed has a cross section of 4" x 8" and rests on a movable tray that can be driven upward at a controlled speed. During the course of an experiment, the bed is continuously moved up to maintain a constant contact geometry with the air supply jet as the surface burns away.

Bed burning "air" is supplied through a slot-jet located just above the apron on the char retaining insert. The width of the slot is

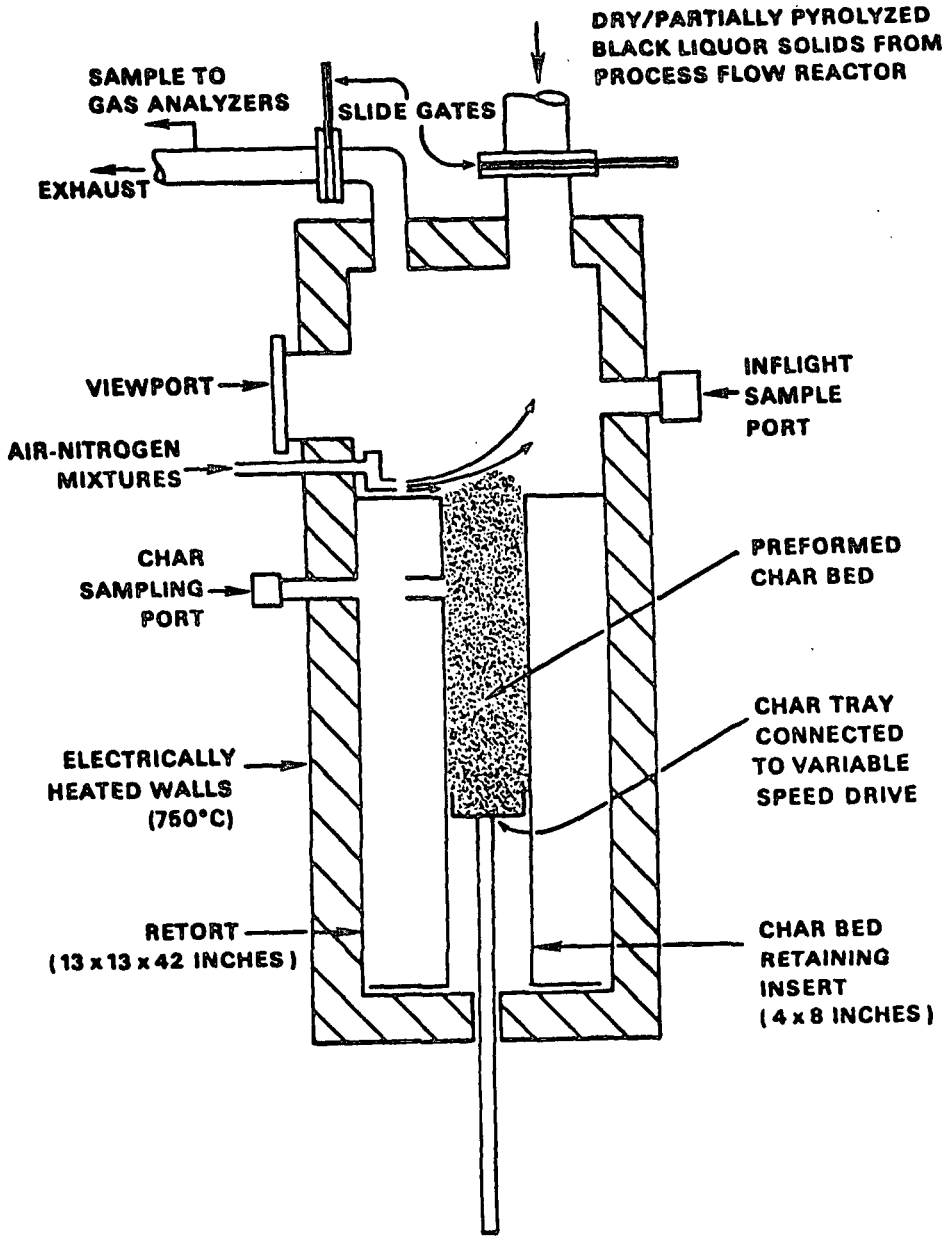



Figure 2. Configuration of Char Bed Burning Furnace.

the same as the width of the char bed (8"). The height of the slot is adjustable. The slot is located 2 1/4" from the leading edge of the char bed. Guides are provided to prevent sideways spreading of the jet. The gas supply to the bed can be heated to a temperature of 250-500oC before it enters the furnace.

The test bed is contained within an electrically heated enclosure. Under operating conditions, the heaters are only capable of reaching 1470oF (800oC). Additional heat generation from char combustion is needed in order to reach higher temperatures.

The char beds used in these tests were formed from pyrolyzed black liquor drops. Pyrolysis of the drops was completed as they sat in the hot (750-800°C) furnace under an inert gas environment for 15 to 45 minutes prior to the start of a char buning experiment. An experiment was begun by changing the gas flow to the slot-jet from pure nitrogen to a mixture of oxygen and nitrogen while starting the mechanism to drive the bed upward at the same time. The bed was observed visually as burning proceeded, and the speed of the drive was adjusted to maintain bed/slot-jet geometry.

The char burning rate was determined from the measured gas flow and the concentrations of CO and $CO_2$ in the product gas. This can be expressed as a carbon flux from the bed by dividing by the nominal cross-sectional area of the bed. The oxygen flux to the bed calculated directly by difference between that

entering and leaving the reactor was always greater than that calculated from the oxygen tied up as CO and $CO_2$. This difference, typically about 0.2 g-moles/min, is believed to be caused by oxidation of metal in the retort and char retainer.

The most useful data were obtained during the constant rate period when the bed was being moved upward to maintain a constant gas-char contact area. Once the limit of bed travel was reached, the rate begins to fall off. The length of the constant rate period depended on the char burning rate. For tests at low velocity and low oxygen concentration, the constant rate period was more than 15 minutes. For high $O_2$ concentrations and high velocities, it was as short as two minutes.

The parameters used in the burning tests with $N_2$ - $O_2$ mixtures were as follows:

| | |
|---|---|
| slot heights | 0.3" and 0.1" |
| gas flow rates | 100, 200, 400, and 550 stdL/min. |
| inlet $O_2$ conc. | 7, 14, and 21% |

The smaller slot height was used to give higher gas velocities at the same flow rate. The effect was less than might first be anticipated. The leading edge of the char bed was 2 1/4" away from the slot, and the scaling factor for the expansion and deceleration of the jet is distance/height. Thus, the test zone is equivalently three times further away for the

small jet, and the jet has expanded and slowed down to a greater extent. In practice, decreasing the slot width by a factor of three only increased the average velocity in the test zone by about 30%.

## BURNING RATE RESULTS

A total of 50 char bed burning runs were carried out for which useful burning rate data were obtained. Burning rates were expressed as carbon fluxes using the measured rates at which carbon left the reactor as CO and $CO_2$ and dividing by the apparent cross-sectional area of the bed. A complete tabulation and description of these experiments is given in Reference 1. Only the results will be presented here.

### Experimental Results

Burning rates were dependent on both the average oxygen concentration over the bed and the gas flow rate. In general, the burning rates were directly proportional to the average $O_2$ concentration over the test zone. One set of data at low velocity showed a linear relationship with a nonzero intercept. The reason for this is unknown. It may be connected with the estimation of the average $O_2$ concentration over the test zone. This was calculated as:

$$O_2ave = [O_2in + (O_2in - O_2 \text{ in carbon gases})]/2$$

The effect of oxygen consumption by reactor components was not included since it was felt that most of this occurred after the jet had swept across the bed surface.

At a given oxygen concentration, the data showed a nearly linear dependence on gas velocity with a positive intercept that was nearly constant. This is consistent with mass transfer controlled burning, since the mass transfer rate would be expected to increase with velocity, and some mass transfer, due to ordinary diffusion, would occur at zero velocity. The linear dependence on velocity is only apparent. The range in velocities covered and the inherent limitations in the data do not allow a reliable estimate of the exponent by statistical techniques.

A linear regression of the large slot burning rate data using the product of O2 concentration and gas flow rate gave an R2 value of 97%, suggesting that the burning rate was proportional to the total oxygen supply. This occurred despite the fact that experimental conditions were deliberately chosen so that the burning rate was not controlled by oxygen stoichiometry. In all cases, significant amounts of oxygen remained in the gas stream after it had passed over the bed.

## Oxygen Mass Transfer Coefficients

Average oxygen mass transfer coefficients, kave, were calculated from the experimental

burning rates by dividing the oxygen flux to the bed by the average oxygen concentration in the gas above the bed zone. The oxygen flux was calculated from the experimentally meas ured carbon flux using the measured ratio of $CO/(CO + CO_2)$ in the gas leaving the reactor. This method assumed that all gas-phase oxidation of CO to $CO_2$ occurred within the mass transfer boundary layer. If some oxidation of CO to $CO_2$ occurred in the gas after it passed the bed surface, the calculated oxygen flux would be over-predicted. Thus, the calculated mass transfer coefficients are maximum values.

The calculated mass transfer coefficients are shown as a function of gas velocity in Figure 3. This figure includes data from both the large slot and small slot experiments. The average gas velocity in the jet over the test zone was calculated using an equation for the centerline velocity of a free turbulent jet from an infinitely wide slot. Experimental measurements were made of gas velocities over the test zone under nonburning conditions using a probe and electronic micromanometer. There was reasonable agreement, especially with the center three test locations. Over-all, predicted velocities were slightly higher than measured velocities, especially at the higher flow rates. There was considerable scatter in measured velocities. There is better alignment between the large slot and small slot mass transfer coefficient data if the free jet expansion equation is used to calculate gas velocities over the test zone rather than an empirical fit of the measured velocities.

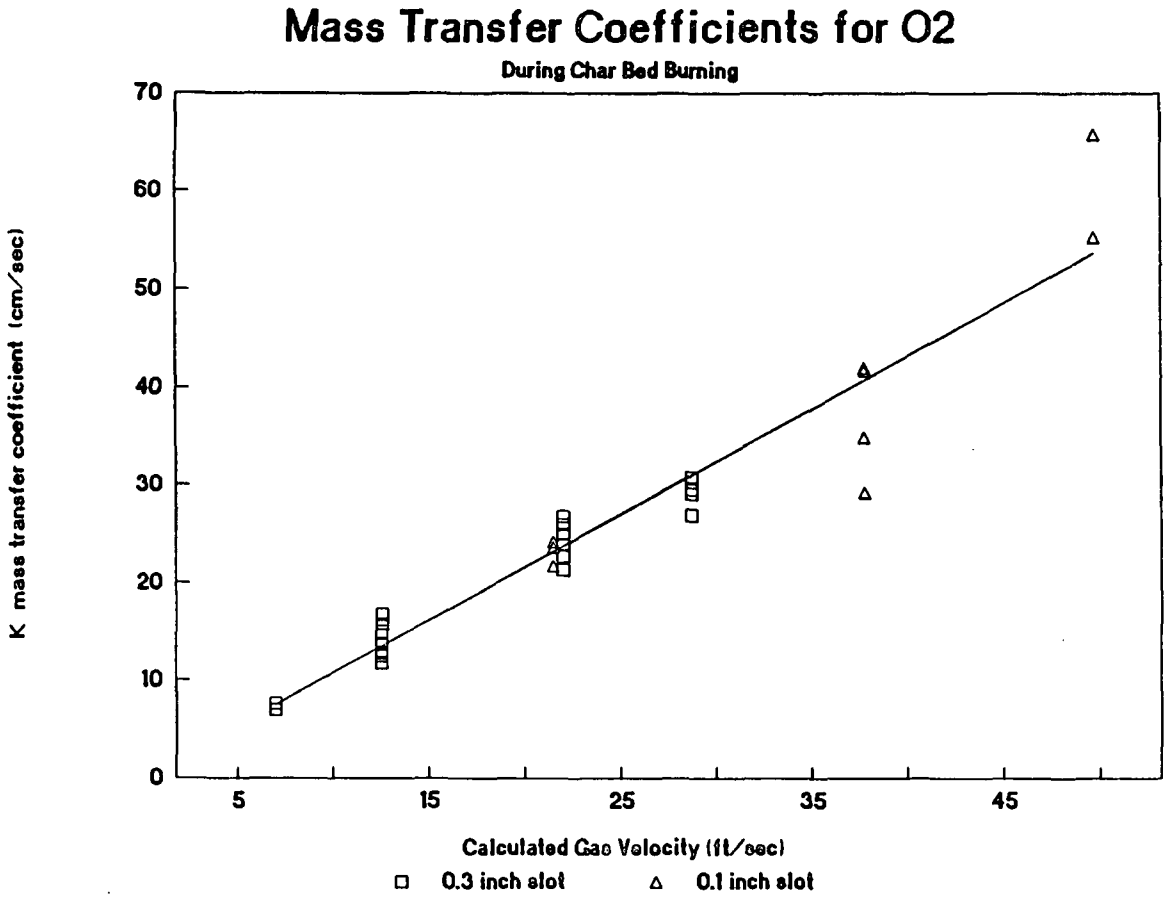



Figure 3. Mass Transfer Coefficients vs. Jet Velocity.

Mass transfer coefficients are normally correlated by dimensionless equations which take the form:

$$Sh = A + B*Re^{n}*Sc^{0.33}$$

where,

Sh = kL/D, Sherwood Number
Re = UL/nu, Reynolds Number
Sc = nu/D, Schmidt Number
k = mass transfer coefficient
L = characteristic length
D = molecular diffusivity
U = characteristic-free stream velocity
nu = kinematic viscosity

A, B, and n are empirical constants. These parameters and the appropriate characteristic dimension depend on the particular geometry of the system.

At first glance mass transfer correlations for flow over a flat plate might seem most appropriate for char bed burning. However, this gives rise to a problem in selecting the characteristic length. If the characteristic length is chosen as the distance along the bed from the air port openings, the mass transfer coefficient would decrease along the bed toward the center of the furnace. This does not appear to be borne out in practice. If a fixed characteristic length is chosen, the choice of a particular value is completely arbitrary.

The mass transfer coefficient data from the laboratory char bed reactor could be fit to

the mass transfer correlation for turbulent flow through a horizontal slit. The applicable equation is:

$$Sh = 0.026*Re^{0.8}*Sc^{0.33}$$

The appropriate slit dimension is the width of the slot-jet over the test zone. This was estimated by assuming the jet expands at a 15° angle as it moves away from the slot. Using a kinematic viscosity of 0.764 $cm^2$/sec and a diffusivity of 0.86 $cm^2$/sec, the predicted mass transfer coefficient equations are (k in cm/sec, U in ft/sec);

$k = 0.35*U^{0.8}$ for the 0.3" slot

$k = 0.36*U^{0.8}$ for the 0.1" slot

These equations need to be adjusted for the fact that the actual bed contact area is greater than the projected flat plane area. A reasonable adjustment factor is 4, the ratio of the surface area of a sphere to the projected circular area. Then the predicted mass transfer coefficient in the test reactor is:

$$k = 1.4*U^{0.8}$$

This prediction can be compared with the lin ear regression equation k = 1.08*U.

$$k = 1.4*U^{0.8} = 1.4*U*U^{-0.2}$$

The range in gas velocities over the test zone in these experiments was from about 6 to 30

ft/sec. Thus, $U^{-0.2}$ would range from 0.7 to 0.5. This is equivalent to k ranging from 0.7*U to 1.0*U. Thus, there is good correspondence between the mass tranfer coefficients predicted by the correlation for turbulent flow in a horizontal slit and those measured in the laboratory reactor.

The analogy to flow through a horizontal slit seems to have applicability to predicting mass transfer to char beds in operating recovery boilers. The "slit width" would be the thick ness of the high velocity gas stream above the bed, and the appropriate velocity would be the average velocity within that width. This concept needs to be pursued further.

## GASIFICATION IN BED BURNING

The essence of bed burning is the conversion of the char carbon in the bed to CO and $CO_2$ gases. The char carbon provides the underly ing structural element for the solid bed material. Removal of the carbon allows the inorganic smelt to become a free-flowing liquid which can collect on the hearth and run out of the furnace. The most direct way to gasify carbon is by reaction with oxygen or with sulfate. However, gasification by reaction with water vapor or carbon dioxide can also be important.

## Gasification Reactions

The reactions that are ordinarily referred to as gasification reactions are as follows:

$CO_2 + C = 2\ CO$ $\quad H = +41.1$ kcal/mol

$H_2O + C = CO + 2\ H_2$ $\quad H = +31.3$ kcal/mol

These are both endothermic heterogeneous reactions that tend to cool the local region of the surface on which they are occurring. Like most heterogeneous reactions, the reaction can be considered as involving mass transfer followed by chemical reaction at the surface in series. The inherent chemical reaction kinetics at the surface have an Arrhenius temperature dependence. If the temperature is high enough, the reaction rates will be mass transfer controlled.

The coupling of an endothermic reaction with Arrhenius temperature dependence means the reaction will tend to be self-limiting unless heat is supplied from an outside source. If heat is available, the reactions can proceed at a mass transfer controlled rate. This is the maximum rate at which the gasification reactions can occur. Gasification could be very important in char bed burning because the concentrations of both $CO_2$ and $H_2O$ vapor are high in the lower furnace.

The role of the gasification reactions can be made clear by treating them in terms of mass transfer and chemical reaction at the surface

in series. The reaction rates for oxygen, water vapor, and carbon dioxide are given by

$R_{O2} = k_{O2} * X_{O2}$

$R_{H2O} = k^{*H2O*X}H_2O \qquad 1/k*H2O = 1/k_{H2O} + 1/K_1e-E_1/T$

$RCO2 = k^{*CO2*X}CO_2 \qquad 1/k*CO_2 = 1/k_{CO2} + 1/K_2e-E_2/T$

where,

k* = apparent rate constant

k = mass transfer coefficient

K1, E1, K2, E1 are chemical kinetic parameters

T = absolute temperature

If the temperature is high enough, the apparent rate constant equals the mass transfer coefficient. The mass transfer coefficients for $O_2$, $H_2O$, and $CO_2$ will vary as the respective diffusivities raise to the 2/3 power. Thus, $k_{H2O}/k_{O2} = 1.3$, and $k_{CO2}/k_{O2} = 0.8$. If it is assumed that the concentrations of $O_2$, $H_2O$, and $CO_2$ are 10%, 20%, and 12%, respectively, the relative reaction rates would be about 1 to 2.6 to 1. Thus, the gasification reactions, if fully active, have the potential of removing more than three times as much carbon from the bed as direct oxidation alone.

It is useful to determine what bed temperatures must be reached for gasification to approach mass transfer control. A characteristic temperature can be defined at which the reaction rate is controlled equally by mass transfer and inherent chemical kinetics. At this temperature, the actual reaction rate will be one half the rate for complete mass

transfer control. For the water gas reaction, this temperature is given by,

$$T_{50} = E_1/\ln(K_1/k_{H2O})$$

A similar expression holds for $CO_2$ gasification It should be noted that the characteristic temperature depends on the mass transfer coefficient as well as the inherent chemical reaction parameters. As the mass transfer coefficient increases (e.g., because of higher velocities), the characteristic temperature increases.

Combined Oxidation/Gasification

Oxidation reactions on or near the bed surface release heat and can raise surface temperatures allowing gasification to proceed. Simultaneous oxidation/gasification can occur when the bed is contacted with a gas stream containing $O_2$, $H_2O$, and $CO_2$. There are two key questions in dealing with combined oxidation/gasification. The first is the extent that gasification and oxidation at the surface occur in parallel. The other has to deal with the overall stoichiometry.

Combined oxidation/gasification can be treated mathematically by defining two parameters.

a = the fraction of oxygen that could react in the boundary layer with CO and $H_2$ evolving off the bed that does react.

f = stoichiometric factor for direct carbon oxidation defined by the reaction

$(1-f/2)O_2 + C = fCO + (1-f)CO_2$

The net oxygen flux to the surface is then given by

$$R'_{O2} = [R_{O2}-a(R_{CO2}+R_{H2O})]/[1+af/(2-f)] \quad R'_{O2}>0$$
$$R'_{O2} = 0 \quad \text{for } R'_{O2} < 0$$

The carbon removal flux, $R_C$, is then given by

$$R_C = R_{CO2} + R_{H2O} + 2/(2-f)*R'_{O2}$$

An interesting special case is a = 1; oxidation proceeds to completion in the boundary layer above the bed. Then

$$R'_{O2} = (2-f)/2*[R_{O2} - R_{CO2} - R_{H2O}]$$
$$R_C = R_{O2}$$
$$\text{if } R_{O2} > R_{H2O} + R_{CO2}$$

and

$$R'_{O2} = 0$$
$$R_C = R_{H2O} + R_{CO2}$$
$$\text{if } R_{O2} < R_{H2O} + R_{CO2}$$

The effect on carbon removal in this case is as if oxidation and gasification are mutually exclusive with the burning rate determined by whether oxygen fluxes or effective $H_2O + CO_2$ fluxes are in excess. In addition, $CO_2$ is the only final product of direct char oxidation, regardless of the actual value of f at the surface.

The opposite extreme is a = 0, no oxidation in the gas phase boundary layer above the bed. In this case, $R'_{O2} = R_{O2}$ and $R_C = R_{O2} + R_{H2O} + R_{CO2}$. The overall stoichiometry will be the net result of the stoichiometry of all three reactions and will depend on the value of f.

A series of experiments on combined oxidation gasification were carried out in the laboratory char bed reactor. These used controlled mixtures of $O_2$, $H_2O$, and $CO_2$ in $N_2$. All of the runs were made at a constant gas flow rate, a slot width of 0.3", and an inlet $O_2$ content of 14%. A 2x2 factorial design was set up testing both $CO_2$ and $H_2O$ at 0 and 10% levels. At least five replicate runs were made at each of the test conditions. Carbon fluxes were determined from the average burning curves for these replicate runs. The results are given in Table 1.

An unweighted means analysis for factorial models indicates that the addition of $CO_2$ at a 10% concentration increased the burning rate by about 25% from 24.4 to 30.3 x $10^{-6}$ gmol/s/$cm^2$. The effect of $CO_2$ is significantly less when water vapor is present. The addition of $H_2O$ at 10% concentration caused a slight drop in the burning rate (from 28.0 to 26.5 x $10^{-6}$). When no $CO_2$ was present, the burning rate was not changed significantly when water vapor was present.

It is well known that water vapor catalyzes the gas phase oxidation of CO. The data are completely consistent with this. The runs

Table 1
Effect of H2O and CO2 on Bed Burning

| H2O | CO2 | Carbon Flux gmol/sec/cm2 | Oxygen Flux gmol/sec/cm2 | CO CO+CO2 | Temp. oC |
|---|---|---|---|---|---|
| 0% | 0% | 24.35 x 10-6 | 19.1 x 10-6 | 0.504 | 961 |
| 0% | 10% | 32.45 " | 23.6 " | 0.638 | 932 |
| 10% | 0% | 24.86 " | 24.7 " | 0.011 | 990 |
| 10% | 10% | 28.09 " | 28.1 " | 0.0 | 967 |

with $H_2O$ present gave negligible amounts of CO in the product gas. In the runs without $H_2O$, CO was a major component of the product gas. Thus, the data indicate that a = 1 in a case with $H_2O$ present such as would be the case in a recovery boiler. This means that oxidation and gasification would tend to be mutually exclusive, with the carbon removal rate determined by whichever rate (oxidation or gasification) was the fastest.

An alternative way to look at gasification effects is to consider the "equivalent oxygen flux" at the bed surface. This can be calculated from the carbon flux using the measured $CO/(CO+CO_2)$ ratio. It should be noted that for the runs in which water was absent, the oxygen flux is less than the carbon flux. When water is present, the oxygen and carbon fluxes are equal.

Analysis of variance for the oxygen flux data indicates that both $H_2O$ and $CO_2$ have a nearly equal effect on the oxygen flux. Addition of 10% $CO_2$ increased the oxygen flux by 24% and addition of 10% $H_2O$ increased it by 29%. The combined effect of $CO_2$ and $H_2O$ is nearly additive.

Since oxygen consumption is a measure of burn ing, the data in Table 2 indicate that $CO_2$ and/or $H_2O$ in the combustion gas stream intensifies combustion very close to the char bed. This would be expected to result in an elevation of bed temperatures which is favor able for bed burning.

Table 2
Char Composition

| Elemental Analysis | wt. % | std. dev. |
|---|---|---|
| Sodium | 29.2 | 1.3 |
| Carbon | 24.9 | 1.0 |
| Hydrogen | 0.57 | 0.09 |
| Oxygen | 35.0 | 0.4 |
| Sulfur | 4.2 | 0.4 |
| Reduction Efficiency, % | 52.6 | 6.0 |
| Bulk Density, g/L | 14.2 | 2.3 |
| Heating Value, kJ/kg | 5260 | 220 |

The average maximum char bed temperature in these oxidation/gasification tests was 962°C. Temperatures were slightly lower when $CO_2$ was present and slightly higher when $H_2O$ was present. At these temperatures, the gasification reactions were not completely mass transfer controlled.

The characteristic temperature range for $CO_2$ gasification can be estimated from the data with no water vapor in Table 1, since gasification and oxidation occurred substantially in parallel in this case. The amount of gasification that occurred with 10% addition of $CO_2$ was $32.45 - 24.35 = 8.1 \times 10^{-6}$ g mol C/cm$^2$/sec. The amount of gasification expected from complete mass transfer control relative to the amount of oxygen mass transfer is $k_{CO2}*X_{CO2}/k_{O2}*X_{O2} = 10/13*0.8 = 0.615$. Thus, the maximum gasification rate from $CO_2$ would be $0.615*24.35 = 15.0 \times 10^{-6}$.

The actual gasification rate was $8.1/15 = 0.54$, which is very close to 50%. Thus, $T_{50}$ for $CO_2$ gasification in these tests in the laboratory char bed reactor was about 930°C. The published data on gasification kinetics for black liquor char (3,4,5) indicates that the value for E1, the activation energy divided by the gas constant, is about 24,000°K. Using this value the temperature for 90% mass transfer control, $T_{90}$, is about 1080°C. Thus, the temperature range over which reaction kinetics affects gasification rates is broad and encompasses the normal range of bed temperatures. If mass transfer coefficients are

increased, the characteristic temperature rises. Doubling the mass transfer coefficient would raise $T_{50}$ by about 45°C. The rate constants for water vapor gasification are somewhat higher, but the activation energy is similar. The water vapor gasification threshold would be somewhat lower, but there would also be a wide range of temperature over which chemical kinetics had some effect on the gasification rate.

## BED COMPOSITION

Char beds in recovery furnaces are very heterogeneous structures. The bottom and interior usually consist primarily of frozen smelt, possibly with channels or pockets of molten smelt. In decanting bottom units, the char bed may be submerged in or even floating on a pool of molten smelt. The upper surface of the bed contains much more carbonaceous material and is usually a good deal more porous. The surface region is where interaction with combustion gases and active burning takes place.

There is very little published information on the composition of char beds in recovery furnaces. Most of the available data were obtained by Merriam and Richardson(7). Their data indicated relatively little carbon in the bed (15-25% of the original carbon). They also found that the density of char bed material ranged from 0.3-1.3 $g/cm^3$.

## Char Composition

All of the laboratory bed burning experiments used char that was produced from a single source of mill black liquor. The chemical and physical characteristics of the char beds were very reproducible. The average chemical composition and standard deviations for char samples taken prior to seven different tests are given in Table 2.

It was observed that bed particles were easily entrained when inert gas (N2) was blown across the bed surface prior to the start of a burn ing test. Once oxygen was admitted and burn ing began, the tendency for entrainment decreased. There were always limits above which the gas velocity could not be increased without entraining particles off the bed.

The composition and density of the char used in these experiments were considerably different from that found by Merriam and Richardson. This does not detract from the validity of the results obtained in this study, but it does indicate that there are processes occurring on the beds in recovery boilers that were not represented in the laboratory bed burning experiments.

All of the char used in these experiments was fully pyrolyzed. This would not be the case in an actual recovery furnace. Some incompletely pyrolyzed liquor solids would normally land on the bed, and this could

represent a significant portion of the fuel delivered to the bed. This will burn in a different mode than the char itself and will affect char burning rates. Pyrolysis is thermally driven, and the gases produced would move upward off the bed. The combustible pyrolysis gases coming off the bed would scavenge oxygen coming toward the bed and thus would affect the rates of heterogeneous char burning in a manner analogous to the way CO and $H_2$ from combined oxidation/gasification affect burning rates. However, in contrast to gasification reactions, the flux of pyrolysis gases would be determined by the rate of heat transfer to the bed and by the amount of pyrolyzable material remaining.

A method for quantitatively treating simultaneous pyrolysis and char burning has not yet been developed. There are also no experimental data on the rate of bed burning under these circumstances. Such data are needed.

## SUBSURFACE REACTIONS

Chemical reactions can also take place beneath the surface of the char bed. It is generally assumed that the bed is impermeable (at least beyond a few cm) to combustion air and gases blowing across it, and so oxidation and gasification reactions below the surface are normally ignored. This is probably a good assumption, although there is a possibility that temperature gradients across the surface of the bed could set up local convection cells

within the bed that could bring $O_2$, $H_2O$, and $CO_2$ below the surface.

There are several reactions however that can take place below the bed surface. These are:

Liquor solids pyrolysis> combustibles + char

$$Na_2SO_4 + 2\,C = Na_2S + 2\,CO_2$$
$$Na_2SO_4 + 4\,C = Na_2S + 4\,CO$$
$$Na_2CO_3 + 2\,C = 2\,Na + 3\,CO$$

All of these are endothermic reactions and cause a drop in temperature below the surface of the bed that slows down the reaction rate. This causes the reactions to become self-limiting. A temperature gradient will be set up within the bed and the amount of reaction that occurs will be dependent on the heat transfer rate into the bed(6).

Modeling of the subsurface reactions in char beds and the extent that they interact with the bed surface reactions is the next step to take in the development of a complete description of char bed burning.

## CONCLUSIONS

1. Bed burning rates in $O_2$ - $N_2$ mixtures are consistent with bed burning being an oxygen mass transfer limited process.

2. Mass transfer coefficients for bed burning can be calculated from conventional mass

transfer correlations. Mass transfer in the char bed reactor is analogous to mass transfer in turbulent flow in a horizontal slit.

3. Gasification of carbon by $CO_2$ and $H_2O$ will be controlled by both mass transfer and chemical kinetics in the range of temperatures normally experienced in char beds.

4. The rate of carbon removal in simultaneous oxidation and gasification is normally equal to the rate of oxygen transfer or to the sum of the effective $CO_2$ and $H_2O$ transfer rates, whichever is greater. Consumption of $O_2$ in the boundary layer by combustibles coming from the bed surface inhibits parallel oxidation and gasification at the bed surface.

5. Gasification reactions enhance the rate of oxygen transfer toward the bed and result in greater oxygen consumption and heat release in the vicinity of the bed.

6. Quantitative descriptions of simultaneous oxidation and gasification are in hand. There remains a need to quantitatively treat the flux of combustibles coming from bed subsurface reactions and pyrolysis on the bed surface.

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